OPTICAL LIMITING MATERIALS BASED ON GOLD NANOPARTICLES

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Final Performance Report: Optical Limiting Materials Based on Gold Nanoparticles

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I. Introduction

A passive optical limiter, a device that ideally allows linear light transmission below a threshold, but above threshold has a constant output intensity, is critical for protection of sensors from laser radiation.[1] The damage threshold for typical sensors and light detectors is $\sim 0.1 - 100$ J/cm^2, depending on irradiation wavelength, pulse duration, and nature of the detector material.[1] Compared to active feedback devices, a passive optical limiting device requires no power, can be made smaller, and might respond faster. The fundamental mechanisms for optical limiting behavior include reverse saturable absorption, multiphoton absorption, free carrier absorption, nonlinear refraction, and nonlinear scattering.[1,2] Third-order nonlinear optical susceptibility is the most important term in the expansion of polarization density, for optical limiting behavior.[1]

Many materials have been explored for their optical limiting behavior, principally carbon black suspensions, organic materials and some semiconductors.[1,2] Recently, metallic nanoparticles have been examined for their optical limiting capabilities: these materials absorb strongly across the visible and near-infrared depending on size, shape, local dielectric environment and degree of aggregation;[3-6] they create large electric fields upon light absorption;[3-6] they undergo multiphoton absorption[7-9] and strongly scatter light both elastically and inelastically.[10-14]

Optical limiting results with gold nanospheres themselves suggest several points of interest: particle size is important, and 25 nm diameter gold nanospheres appear to be superior for optical limiting compared to smaller and larger spheres;[15,16] pushing the strong visible plasmon absorption of gold nanospheres into the near-infrared by aggregating them increases their optical limiting capabilities (although fusion of particles into needle-shaped ones might be responsible);[17] and chromophores that may already be of interest for their nonlinear optical properties have those properties enhanced by the presence of metal nanoparticles (although there is some conflicting data in the literature).[18] The suggested mechanism(s) for the optical limiting capabilities of gold nanoparticles include nonlinear scattering and free carrier absorption.[15-18] Overall, the data in the literature is tantalizing, and suggests that a concerted effort to explore the optical limiting capabilities of gold nanoparticles as a function of size, shape, aggregation state, and in the presence of interesting chromophores, is needed.

II. Statement of Objectives

The objectives of this proposal were to (i) understand how the nonlinear optical properties of chromophores are altered in the presence of nanoscale metal particles; and (ii) assess the ability of gold nanoparticle-chromophore conjugates to function as optical limiters.

We proposed several tasks to achieve these objectives:

1. Synthesis and characterization of a library of colloidal gold nanoparticles of well-defined size and shape, optimized for strong absorption in the visible and near-infrared portions of the electromagnetic spectrum.

2. Functionalization of the surface of the gold nanoparticles with selected organic and inorganic materials, with well-defined nanoscale thicknesses, and characterization of these hybrid systems thoroughly by electron microscopy, light scattering, steady-state electronic absorption spectroscopy, steady-state fluorescence spectroscopy, zeta potential analysis, Fourier-transform infrared spectroscopy, and inductively-coupled plasma atomic emission spectroscopy upon digestion (to quantitate metal). Further derivatization of these materials with selected chromophores to place the chromophore at well-defined distances from the nanoscale metal surface is a critical step.

3. Characterization of the nonlinear optical properties of the colloidal gold nanoparticles, both native and coated with the spacer materials/chromophores, in solution, in collaboration with AFRL/RXPJ, by time-resolved fluorescence, ultrafast pump-probe (femtosecond), flash photolysis (nanosecond), and Z-scan, to determine the impact of gold nanoparticle additives on nonlinear optical properties.

4. Fabrication of thin films of these materials on glass slides using layer-by-layer deposition techniques, or embedding of the materials in thick polymer films that can be deformed and so crudely align the particles.

5. Comparison of the nonlinear optical responses of thin films of the materials to each other and to different particle densities and distances within the films.

The proposed research was a collaboration between Catherine J. Murphy of the University of South Carolina and the Agile Limiters research group in AFRL/RXPJ of the Wright-Patterson Air Force Base. Murphy moved to the University of Illinois at Urbana-Champaign in the summer of 2009; therefore, the award was modified so that her former department chair, John Dawson, became the PI of the award, with Murphy as a subcontract at UIUC. Murphy was responsible for the synthesis and characterization of the gold nanoparticles and their surface functionalization. AFRL was responsible for the time-resolved and multiphoton optical measurements. Murphy's unique capabilities included synthesis of an enormous range of gold and silver nanomaterials (spheres, rods, wires, cubes, tetrapods, needles, etc. of varying dimensions) and the Agile Limiters group has unique capabilities to characterize exotic nonlinear optical materials of scientific interest and with relevance to Air Force applications. Murphy and her students visited the

Wright-Patterson Air Force Base to meet with the Agile Limiters Group approximately once per year.

III. Relevance to the Air Force Office of Scientific Research

The area of "complex materials and structures" is one of the five focus areas of "The Future Air Force" as defined by the Broad Agency Announcement for 2008. Within this area, control of optical properties such as refractive index and multiphoton absorption are of interest. The optical limiting application mentioned in the Introduction is part of warfighter and equipment protection, but intriguing new ideas on gold nanoparticle-based metamaterials offer the possibility that some of the structures described below might be useful for negative refractive index ("cloaking") applications.[19]

IV. Technical Results

After creating a library of gold nanoparticles that absorbed and scattered light at controllable wavelengths (2009-2010), developing a "capture coat" method to electrostatically trap chromophores at defined distances from the metal surface (2009-2010), identifying and functionalizing the chromophores properly (2010-2011), we measured the plasmonic enhancement of the two-photon absorption (TPA) cross-section of organic chromophores attached to polyelectrolyte-coated gold nanorods (Figure 1).[20, 21] The attachment procedures were based on electrostatics, using layer-by-layer polyelectrolyte wrapping to flip the effective surface charge of the gold nanorods.[22] The organic chromophores were derivatized with ionic groups so that they would be deposited electrostatically around the gold nanorods (Figure 2).
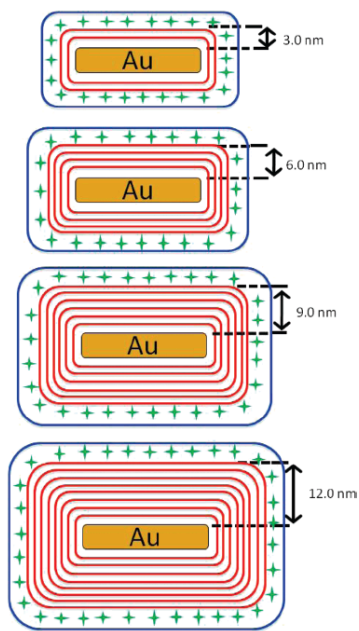

Figure 1. *Schematic of polyelectrolyte layer-by-layer assembly of gold nanorods, bearing original CTAB surfactant layer, with commercially available cationic and anionic polyelectrolyte spacer layers (red), followed by a layer of the organic chromophore (green stars) with a final polyelectrolyte trap coat (blue). The indicated distances are nominal ones from the surface of the CTAB bilayer, which adds 3 nm to the overall distance from the metal surface.*
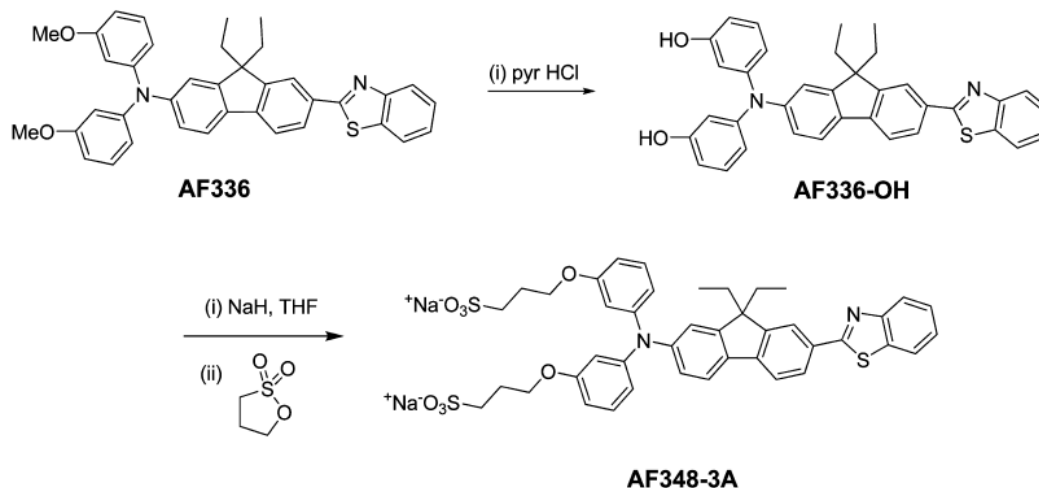
Figure 2. *Synthesis of AF348-3A, a charged derivative of the AF336 two-photon absorbing chromophore.*

Quantification of the number of chromophores per nanorod was performed by a combination of chemical digestions and extractions from the chromophore/nanorod assemblies and liquid chromatography/mass spectrometry analysis (Figure 3).
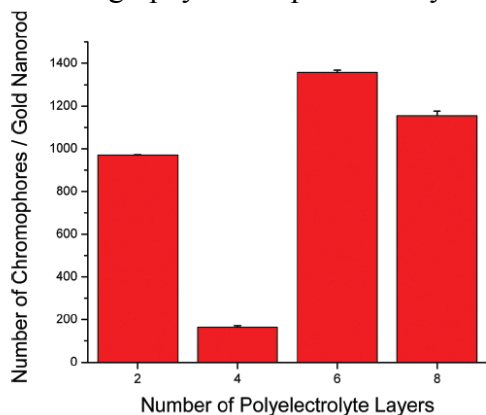

Figure 3. *Number of AF-348-3A chromophores per gold nanorod. Error bars correspond to one standard deviation from the mean of 3-6 measurements.*

For these systems, in which both chromophore and nanorods absorbed maximally at the laser wavelength of 785 nm, we discovered that the TPA cross-section of the chromophores was enhanced 40-fold, for the closest distance between the gold surface and the dye.[20] As the distance increased, the enhancement dropped off in accord with the calculated electric field of the plasmonic nanoparticle (Figure 4).
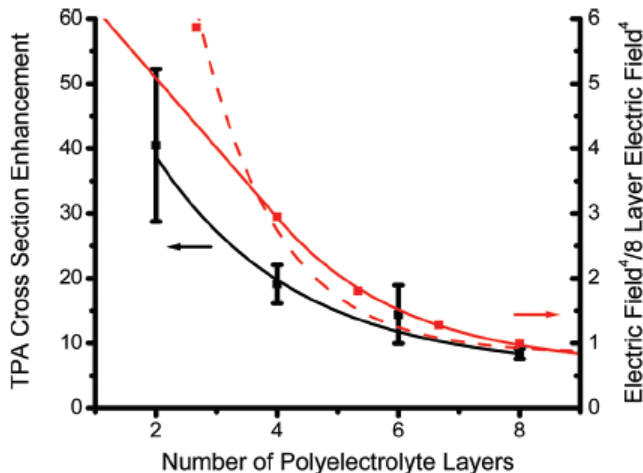
Figure 4. Two-photon cross-section enhancement of the chromophore (signal on the resonant nanorod, divided by the signal off the nanorod) as a function of layer spacing (black dots; black line is a guide to the eye). The red data points show the calculated electric field due to plasmonic excitation of the nanorods, either including (solid red line) or not including (dashed red line) the closest distance.

In these experiments, the two-photon cross-section enhancement is defined as the ratio of the two-photon absorption cross section of the chromophore on the gold nanorods to the two-photon absorption cross section without gold nanorods, where the two-photon cross section is defined according to Equation 1:

$$\sigma^{(2)} = \sigma^{(1)} \frac{\phi_{2\omega} I(\text{2PL})}{\phi_\omega^2 I(\text{1PL})}$$

Equation 1

The $\sigma^{(2)}$ was determined using the method of Hermann and Ducuing, which compares the one photon fluorescence resulting from a known absorption cross-section to the two photon fluorescence arising from an unknown absorption-cross section.[23]

This method calculates $\sigma^{(2)}$ according to eq 1, where $\sigma^{(1)}$ is the one-photon absorption cross-section, and ϕ_{2w} and ϕ_w are the flux densities (photons/m^2-s) of the single-photon, and two-photon excitation beams, respectively. The intensity maximum of the two photon fluorescence is described by I(2PL) and likewise for the single photon fluorescence. Since a one photon cross-section can be calculated with relative ease, eq 1 relates the single photon fluorescence intensity of a molecule with a known one-photon absorption cross-section to the two-photon fluorescence intensity of the same molecule with an unknown two photon absorption cross-section.

In contrast, when the dye TPA spectrum was off resonance compared to the nanorod plasmon resonance (specifically, laser wavelength of 785 nm, dye resonance at 785 nm, but plasmon maximum at 650 nm), a difficult-to-interpret distance dependence of the TPA cross-section enhancement was observed: the TPA *decreased* then *increased* as the dye-gold distance increased (Figure 5). This seemingly bizarre result was in accord with the calculated distance dependence of the electric field from the off-resonance plasmon (Figures 5, 6).[21] The picture that emerges from these results is the gold nanoparticle/chromophore system can be described as a collection of coupled oscillators with complex on- and off-resonance behavior. The

inputs into this system include the optical excitation frequency, gold nanoparticle geometry (rods, spikes, dogbone), nanoparticle resonances, chromophore resonances and gold nanoparticle/chromophore geometric relationships. The outputs from this system include two-photon cross-section, excited state kinetic behavior, constructive/destructive interference of energy flow through a plasmonic circuit, and optical switching behavior.
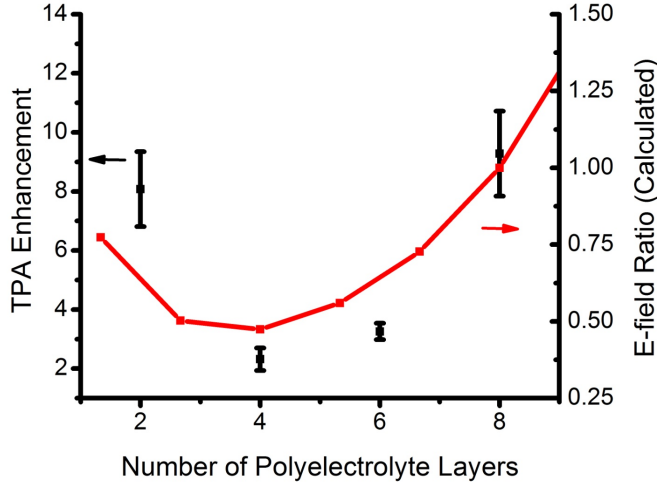

Figure 5. *Measured two-photon absorption cross-section enhancement (left axis, black points) and the calculated electric field ratio of layer n to layer 8 (right* axis, red points) *for aspect ratio 2 polyelectrolyte-bearing gold nanorods complexed with the AF348-3A chromophore, as a function of number of spacer layers. The red line is drawn only to aid the eye.*
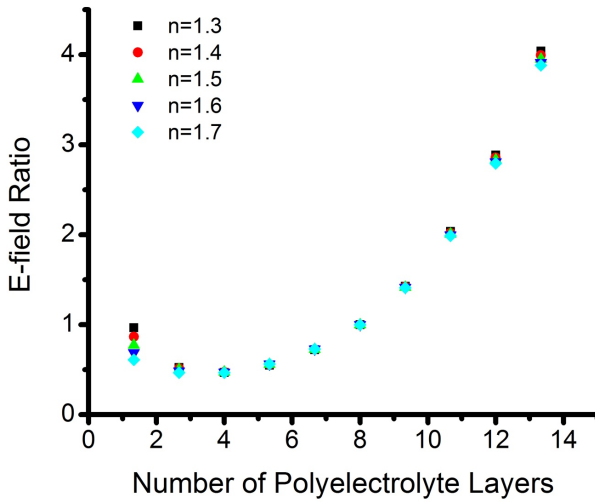

Figure 6. *Electric field ratio of aspect ratio 2 gold nanorods, for layer n divided by layer 8, calculated using COMSOL Multiphysics for different refractive indices n:* ■*, n = 1.3;* ●*, n = 1.4;* ▲*, n = 1.5;* ▼*, n = 1.6;* ♦*, n = 1.7.*

We demonstrated that the same polyelectrolyte wrapping that enabled chromophore placement as a function of distance on the gold nanorods also enabled nanorod incorporation into polymer matrices, a prerequisite for making thin film optical devices from these nanomaterials (Figure 7).[24]
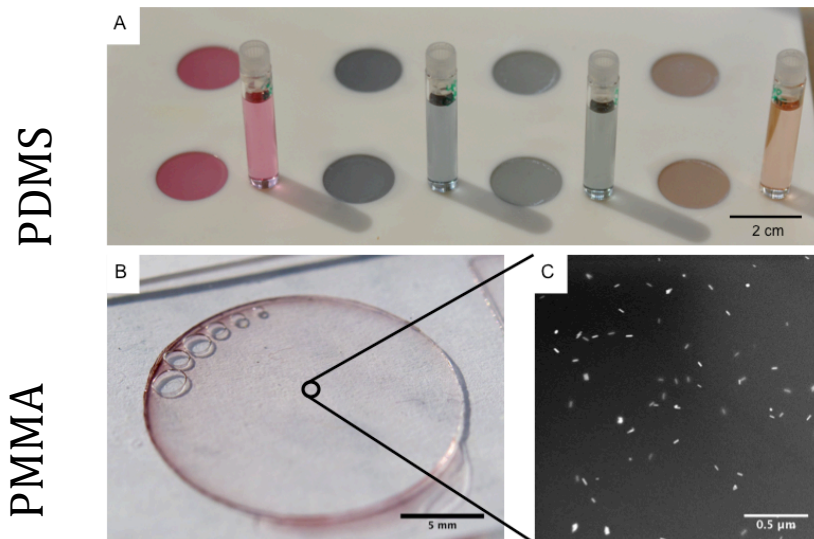
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Figure 7. *(a) Photographs of aqueous solutions of 1 nM various aspect ratio gold nanorods and their corresponding PDMS films, illustrating that the same plasmonic optical properties are retained in the film, even for film concentrations that are 50x higher than possible in solution. (b) Photograph of gold nanorod-PMMA composite film. (c) Cross sectional scanning electron micrograph of the gold nanorod-PMMA composite, showing well-dispersed nanorods.*

In addition, we have learned that some of the same issues important in TPA properties of chromophores are relevant to surface-enhanced Raman scattering chromophores; details are in the published papers that are listed later.

Calculation of the electric field around the nanorods, on resonance, indicates that the (i) closer to the surface shows the largest fields, and (ii) the ends of the rods are "hotter" than the sides.
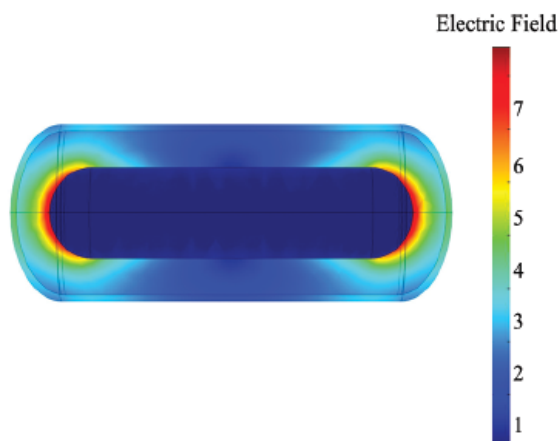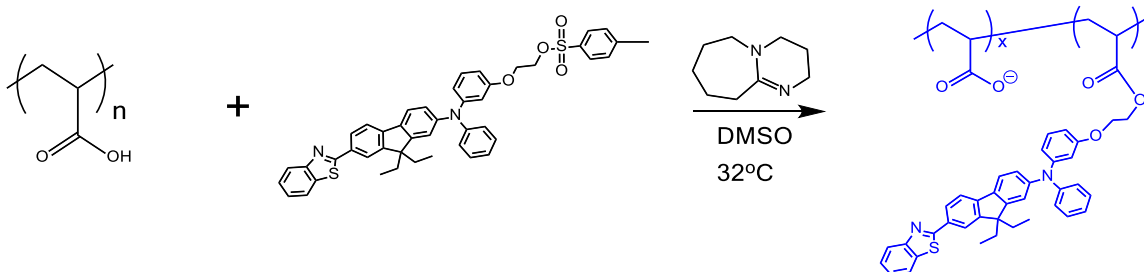

Figure 8. *Calculation of the electric field due to longitudinal plasmon band excitation of a gold nanorod.*

Figure 8. *Calculation of the electric field due to longitudinal plasmon band excitation of a gold nanorod.*

Therefore, in the last year (2012-present), we have begun to explore strategies to robustly functionalize only the ends of gold nanorods with chromophores, and to bring the chromophores even closer to the metal surface. In one scheme, chromophores were functionalized as pendant species on the polyelectrolytes used to wrap the nanoparticles, so as to enable the chromophores to insert into the initial surfactant bilayer on the nanorods and therefore be even closer to the metal surface:

Scheme 1. *Synthetic scheme to attach dye AF240-Tos to polyacrylic acid in the presence of base to create dye-modified polymers for subsequent nanorod wrapping.*

NMR and UV-vis characterization confirmed that approximately 3 dyes were attached per chain, for molecular weight 15,000 g/mol polyacrylic acid. This was desirable to reduce chromophore-chromophore interactions on the nanorods that might quench photophysical processes.

Wrapping of gold nanorods, longitudinal plasmon band maximum at 785 nm, with the dye-modified polymer (DMP) proceeded as per Figure 1. Uv-vis spectra (Figure 9) and zeta potential measurements confirmed proper wrapping up to 9 layers out.
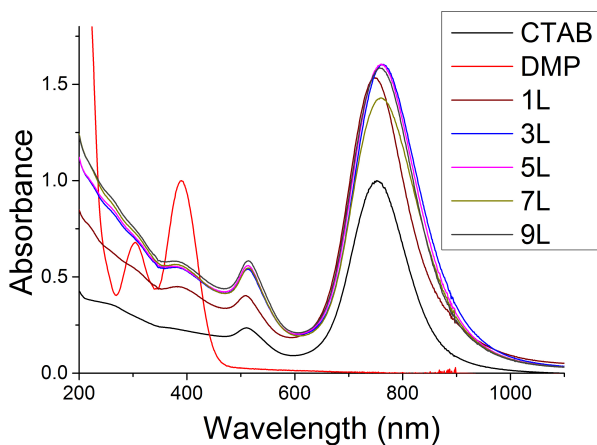

Figure 9. *UV-vis spectra of the DMP alone (red), and gold nanorods with the native CTAB coating (black) or DMP-coated rods with the indicated number of spacer layers between the chromophores and the metal surface.*

Two-photon spectra of the DMP samples were taken by Dr. Jarrett Vela, RYDP/Wyle (formerly part of the Agile Limiters team), Wright-Patterson Air Force Base. These preliminary data suggest that there is no distance dependence for two-photon cross-section enhancement in these systems (Figure 10).
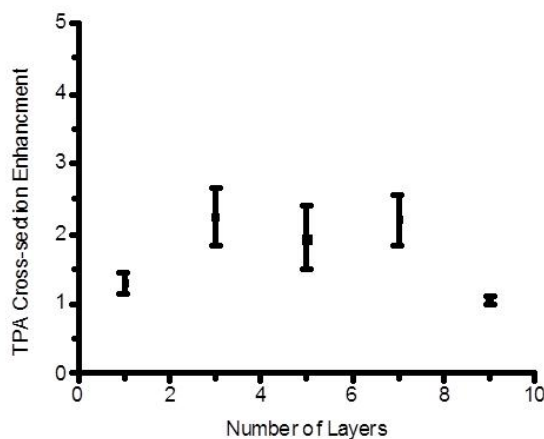

Figure 10. Measured two-photon absorption cross-section enhancement for aspect ratio 4 polyelectrolyte-bearing gold nanorods complexed with the DMP as a function of number of spacer layers.

There are numerous explanations for this surprising result. One cause could be sample robustness: it is difficult to absolutely measure the distance between chromophore and metal surface, and perhaps the DMP was able to "burrow" in and so no layer dependence was observed. This may explain the lack of distance dependence in the data, but it does not explain why there is no enhancement in the two-photon cross-section. It is also possible that anchoring the chromophore to the polymer altered its orientation relative to the longitudinal dipole, and so even if the chromophore was present at defined distances from the surface, it was unable to couple to the plasmon and so no enhancement in two-photon absorption was observed. In the remaining weeks of the award, we will attempt to work out the answer(s).

V. Products: Human Resources and Publications

The previous funding period (March 1, 2009 – May 15, 2014) supported the thesis work of one Ph.D. student (Sean Sivapalan, Ph.D. in materials science and engineering, graduated in 2013, now employed at Intel; currently Jonathan Eller, Ph.D. student in chemistry), and partially supported the work of several other students or postdocs in the lab. The following publications were support by the previous funding period:

- Murphy, C. J.; Thompson, L. B.; Alkilany, A. M.; Sisco, P. N.; Boulos, S. P.; Sivapalan, S.; Yang, J. A.; Chernak, D. J.; Huang, J. "The Many Faces of Gold Nanorods," *J. Phys. Chem. Lett.* **2010**, *1*, 2867-2875.
- Alkilany, A. M.; Thompson, L. B.; Murphy, C. J. "Polyelectrolyte Coating Provides a Facile Route to Suspend Gold Nanorods in Polar Organic Solvents and

Hydrophobic Polymers," *ACS Appl. Mater. & Interfac.* **2010**, *2*, 3417-3421.

- Murphy, C. J.; Thompson, L. B.; Chernak, D. J.; Yang, J. A.; Sivapalan, S. T.; Boulos, S. P.; Huang, J.; Alkilany, A. M.; Sisco, P. N. "Gold Nanorod Crystal Growth: From Seed-Mediated Synthesis to Nanoscale Sculpting," *Curr. Opin. Colloid. Interfac. Sci.* **2011**, *16*, 128-134.

- Sivapalan, S. T.; Vella, J. H.; Yang, T. K.; Dalton, M. J.; Swiger, R. N.; Haley, J. E.; Cooper, T. M.; Urbas, A. M.; Tan, L-S.; Murphy, C. J. "Plasmonic Enhancement of the Two Photon Absorption Cross Section of an Organic Chromophore using Polyelectrolyte-coated Gold Nanorods," *Langmuir* **2012**, *28*, 9147-9154.

- Sivapalan, S. T.; Vella, J. H.; Yang, T. K.; Dalton, M. J.; Haley, J. E.; Cooper, T. M.; Urbas, A. M.; Tan, L.-S.; Murphy, C. J. "Off-resonance Two-Photon Absorption Cross Section Enhancement of an Organic Chromophore on Gold Nanorods," *J. Phys. Chem. Lett.* **2013**, *4*, 749-752.

- van Dijk, T.; Sivapalan, S. T.; DeVetter, B. M.; Yang, T. K.; Schulmerich, M. V.; Murphy, C. J.; Bhargava, R.; Carney, P. S. "Competition Between Extinction and Enhancement in Surface-Enhanced Raman Spectroscopy," *J. Phys. Chem. Lett.* **2013**, *4*, 1193-1196.

- Sivapalan, S. T.; DeVetter, B. M.; Yang, T. K.; Schulmerich, M. V.; Bhargava, R.; Murphy, C. J. "Surface-enhanced Raman Spectroscopy of Polyelectrolyte-Wrapped Gold Nanoparticles in Colloidal Suspension," *J. Phys. Chem. C* **2013,** *117*, 10677-10682.

- Sivapalan, S. T.; DeVetter, B. M.; Yang, T. K.; van Dijk, T.; Schulmerich, M. V.; Carney, P. S.; Bhargava, R.; Murphy, C. J. "Off-resonance Surface-Enhanced Raman Spectroscopy from Gold Nanorod Suspensions as a Function of Aspect Ratio: Not What We Thought," *ACS Nano* **2013**, *7*, 2099-2105.

- Shah, A. B.; Sivapalan, S. T.; DeVetter, B. M.; Yang, T. K.; Wen, J.; Bhargava, R.; Murphy, C. J.; Zuo, J-M. "High-Index Facets in Gold Nanocrystals Elucidated by Coherent Electron Diffraction," *Nano Lett.* **2013**, *13*, 1840-1846.

Bibliography

1. Tutt, L. W.; Boggess, T. F. A Review of Optical Limiting Mechanisms and Devices Using Organics, Fullerenes, Semiconductors and Other Materials. *Prog. Quant. Electr.* **1993**, *17*, 299-338.

2. Mishra, S. R.; Mehendale, S. C. Organic Materials for Optical Limiting. in *Handbook of Advanced Electronic and Photonic Materials and Devices: Volume 9, Nonlinear Optical Materials*, Nalwa, H. S., Ed.; Academic Press, 2001.

3. El-Sayed, M. A. Some Interesting Properties of Metals Confined in Time and Nanometer Space of Different Shapes. *Acc. Chem. Res.* **2001**, *34*, 257-264.

4. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape and Dielectric Environment. *J. Phys. Chem. B* **2003**, *107*, 668-677.

5. Daniel, M-C.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications Towards Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2004**, *104*, 293-346.

6. Murphy, C. J.; Sau, T. K.; Gole, A.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. Li, T. Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. *J. Phys. Chem. B* **2005**, *109*, 13857-13870.

7. West, R.; Wang, Y.; Goodson III, T. Nonlinear Absorption Properties in Novel Gold Nanostructure Topologies. *J. Phys. Chem. B* **2003**, *107*, 3419-3426.

8. Farrer, R. A.; Butterfield, F. L.; Chen, V. W.; Fourkas, J. T. Highly Efficient Multiphoton-Absorption-Induced Luminescence from Gold Nanoparticles. *NanoLett.* **2005**, *5*, 1139-1142.

9. Lippitz, M.; van Dijk, M. A.; Orrit, M. Third-Harmonic Generation from Single Gold Nanoparticles. *NanoLett.* **2005**, *5*, 799-802.

10. Feldheim, D. L.; Foss, C. A., Jr., Editors. *Metal Nanoparticles: Synthesis, Characterization and Applications*; Marcel Dekker: New York, 2002.

11. Raschke, G.; Kowarik, S.; Franzl, T.; Sonnichsen, C.; Klar, T. A.; Feldmann, J.; Nichtl, A.; Kurzinger, K. Biomolecular Recognition Based on Single Gold Nanoparticle Light Scattering. *NanoLett.* **2003**, *3*, 935-938.

12. Orendorff, C. J.; Gearheart, L. A.; Jana, N. R.; Murphy, C. J. Aspect Ratio Dependence on Surface Enhanced Raman Scattering Using Silver and Gold Nanorod Substrates. *PhysChemChemPhys* **2006**, *8*, 165-170.

13. Mock, J. J.; Barbic, M.; Smith, D. R.; Schultz, D. A.; Schultz, S. Shape Effects in Plasmon Resonance of Individual Colloidal Silver Nanoparticles. *J. Chem. Phys*. **2003**, *116*, 6755-6759.

14. Pelton, M.; Liu, M. Z.; Park, S.; Scherer, N. F.; Guyot-Sionnest, P. Ultrafast Resonant Optical Scattering from Single Gold Nanorods: Large Nonlinearities and Plasmon Saturation. *Phys. Rev. B* **2006**, *73*, art. no. 155419.

15. Francois, L.; Mostafavi, M.; Belloni, J.; Delaire, J. A. Optical Limitation Induced by Gold Clusters: Mechanism and Efficiency. *Phys. Chem. Chem. Phys*. **2001**, *3*, 4965-4971.

16. Gao, Y.; Chang, Q.; Ye, H.; Jiao, W.; Li, Y. H.; Wang. Y.; Song, Y.; Zhu, D. Size Effect of Optical Limiting in Gold Nanoparticles. *Chem. Phys*. **2007**, *336*, 99-102.

17. Wang, G.; Sun, W. Optical Limiting of Gold Nanoparticle Aggregates Induced by Electrolytes. *J. Phys. Chem. B* **2006**, *110*, 20901-20905.

18. Wang, Y.; Xie, X. B.; Goodson III, T. Enhanced Third-Order Nonlinear Optical Properties in Dendrimer-Metal Nanocomposites. *NanoLett*. **2005**, *5*, 2379-2384.

19. Shalaev, V. M. Optical Negative-Index Metamaterials. *Nature Photonics* **2007**, *1*, 41-48.

20. Sivapalan, S. T.; Vella, J. H.; Yang, T. K.; Dalton, M. J.; Swiger, R. N.; Haley, J. E.; Cooper, T. M.; Urbas, A. M.; Tan, L-S.; Murphy, C. J. Plasmonic Enhancement of the Two Photon Absorption Cross Section of an Organic Chromophore using Polyelectrolyte-coated Gold Nanorods. *Langmuir* **2012**, *28*, 9147-9154.

21. Sivapalan, S. T.; Vella, J. H.; Yang, T. K.; Dalton, M. J.; Haley, J. E.; Cooper, T. M.; Urbas, A. M.; Tan, L.-S.; Murphy, C. J. Off-resonance Two-Photon Absorption Cross Section Enhancement of an Organic Chromophore on Gold Nanorods. *J. Phys. Chem. Lett*. **2013**, *4*, 749-752.

22. Gole, A.; Murphy, C. J.: Polyelectrolyte-coated Gold Nanorods: Synthesis, Characterization and Immobilization. *Chem. Mater.* **2005**, *17*, 1325-1330.

23. Hermann, J. P.; Ducuing, J.: Absolute Measurement of Two-Photon Cross Sections. *Phys. Rev. A* **1972**, *5*, 2557-2568.

24. Alkilany, A. M.; Thompson, L. B.; Murphy, C. J. Polyelectrolyte Coating Provides a Facile Route to Suspend Gold Nanorods in Polar Organic Solvents and Hydrophobic Polymers. *ACS Appl. Mater. & Interfac*. **2010**, *2*, 3417-3421.